

AN INTEGRATED APPROACH FOR ASSESSING THE POTENTIAL PRESENCE AND DISTRIBUTION OF DNAPLs AT A SUPERFUND SITE IN NEW JERSEY

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Abstract

Dense non-aqueous phase liquids (DNAPLs) are common contaminants at many industrial sites across the United States. DNAPLs not only persist in the soils, but they can also serve as on-going, persistent sources for ground water contamination. Industry and the United States Environmental Protection Agency (USEPA) alike recognize the difficulty, and in some cases "technical impracticability", of remediating DNAPL source areas, particularly in the saturated zone. Determining whether or not DNAPLs are present at a site, and their spatial distribution, is essential in evaluating potential remedial or containment technologies. Large databases of quantitative and qualitative data exist for many suspected DNAPL sites, whereas physical evidence of DNAPLs is often limited. This paper presents an integrated approach to assess a site for the potential presence and distribution of DNAPLs using existing site data. Both ground water and soil quality data were evaluated to determine the potential presence of DNAPLs using various screening methods. These methods included USEPA guidance procedures for evaluating ground water quality data, a method after Feenstra, et al. (1991) for evaluating soil quality data, a site-specific head-space correlation, and visual observations. The database consisted of more than 1,200 analytical soil sample results, nearly 10 years of ground water quality monitoring data from more than 400 monitoring wells, over 800 soil boring logs, and more than 5,000 head-space analyses. Evaluation of the existing data resulted in the demarcation of a "Preliminary DNAPL Boundary", which was considered to represent the likely outer extent of any significant DNAPLs that could serve as an ongoing source of ground water contamination. Using an integrated approach to assess the potential presence and distribution of DNAPLs at a site by evaluating existing data can serve to focus and streamline any additional DNAPL investigations.

Introduction

Dense non-aqueous phase liquids (DNAPLs) are widely recognized by both industry and regulators as one of the most significant issues to be addressed when investigating hazardous waste sites. Not only do DNAPLs persist in soils, serving as a potential exposure risk, but they can also serve as a long-term source for ground water contamination. As long as significant quantities of residual DNAPLs are present and contributing to a dissolved-phase ground water contaminant plume, even the most well-designed ground water remediation system cannot be expected to "cleanup" the entire plume in a reasonable time frame. With the overall remedial objective at many sites being "aquifer restoration", the presence of DNAPLs can present a difficult dilemma to overcome. Therefore, determining whether or not DNAPLs are present at a site, and their spatial distribution, is essential in evaluating potential remedial or containment technologies.

The DNAPLs' counterparts, LNAPLs (light non-aqueous phase liquids) also are present at many industrial sites; however, since they accumulate atop the uppermost saturated zone, they do not present the same challenges with respect to delineation and remediation as DNAPLs.

This article presents a case study where an integrated approach was utilized to evaluate existing site data and assess the site for the potential presence and distribution of DNAPLs. This assessment was the initial component of a "NAPL Action Plan" developed for the site, as required by the United States Environmental Protection Agency (USEPA) in the Consent Decree administered for the site. Both DNAPLs and LNAPLs were targeted with the integrated approach; however, since the potential for DNAPLs was much greater at the site, they are the focus of this article.

The study site is a Superfund site in New Jersey underlain by the Cohansey Sand of the New Jersey Coastal Plain. The site is situated on approximately 1,400 acres, with the former manufacturing facilities occupying approximately 300 acres of the total. The undeveloped portion of the site is wooded, consistent with the pine barrens character of the region. The site is bounded on the east and northeast by the Toms River, while the remainder of site is bounded by residential and light commercial areas. The layout of the site is illustrated on Figure 1, as well as the primary potential DNAPL source areas.

The database used in this case study consisted of three primary types of data collected over the last 10 years: analytical data, soil boring logs, and head-space analysis results (from soil samples). More than 1,200 analytical soil sample results and more than 7,000 analytical ground water sample results from over 400 monitoring wells on site were evaluated. More than 800 soil boring logs were reviewed and over 5,000 head-space results were also included in the database.

This article focuses on the integrated approach developed to assess the site for DNAPLs using available existing data. As such, the interpretative results obtained through applying the integrated approach are not presented in great detail. Sufficient detail, however, is provided to allow the validity of the approach to be tested, as well as its potential applicability to other sites. Greater detail regarding the results obtained through specific components of the integrated approach are anticipated to be provided in future articles.

Geologic Setting

The site is situated within the Atlantic Coastal Plain physiographic province and is underlain by a complex stratigraphic sequence of largely unconsolidated sands, silts, and clays of Cretaceous, Tertiary, and Quaternary age. These transgressive and regressive sequences of unconsolidated sediments vary in thickness from zero at the northern boundary with the New Jersey Piedmont, to greater than 6,000 feet in the vicinity of Cape May at the extreme southeastern tip of New Jersey. Locally at the site, the coastal plain sequence has been shown to be over 2,250 feet thick, typically striking northeast-southwest and dipping gently to the southeast. The Coastal Plain sediments that are of significance to this case study are those which occur within the upper 250 feet of the sequence. These include the Tertiary age sediments of the Kirkwood and Cohansey formations. These formations have been informally subdivided into seven hydrostratigraphic units consisting of four aquifers and three aquitards. The stratigraphic relationship and nomenclature of each unit are presented on Figure 2. The hydraulic conductivity of the aquifers beneath the site is generally on the order of 5.0×10^{-2} cm/sec (140 ft/day), whereas the aquitards' vertical hydraulic conductivity is typically on the order of 5.0×10^{-4} cm/sec (1.4 ft/day) to 5.0×10^{-6} cm/sec (1.4×10^{-2} ft/day). The Primary Cohansey Aquifer is the regional water table aquifer and its water table surface is typically encountered beneath the site at depths ranging from 30-40 feet below ground surface.

The Yellow Clay lies within the unsaturated zone in the western portion of the site and generally dips to the east where it intersects and dips below the Primary Cohansey Aquifer water table. The Yellow Clay is discontinuous beneath the site. Where present, it is usually encountered between 20 and 30 feet below ground surface. It typically ranges in thickness from less than one foot to ten feet, with a vertical hydraulic conductivity of approximately 5×10^{-8} cm/sec (1.4×10^{-4} ft/day). Locally, perched ground water occurs atop the Yellow Clay. The lateral extent and saturated thickness of the perched ground water are controlled by recharge from precipitation events and the geometry of the clay surface. The perched ground water flow generally follows the slope of the clay surface until it intersects the regional aquifer or flows through a structural outlet (Howard and Watkins, 1991).

DNAPL Behavior in the Subsurface

When DNAPLs are released to the subsurface from a spill, a leaking underground storage tank, or from other types of disposal, they tend to move vertically downward through the unsaturated, or vadose zone. Although the net direction of movement will be downward, considerable lateral spreading can occur as the DNAPLs preferentially follow pathways offering less capillary resistance. The result is a complex pattern of DNAPL movement even in apparently homogeneous sands. Poulsen and Kueper (1991) have documented such patterns in their field studies.

As DNAPLs move downward through the unsaturated zone, in most cases following a system of complex pathways as illustrated in the Poulsen and Kueper studies, they leave behind a residual saturation of DNAPLs in the porous medium. This residual saturation consists of a myriad of DNAPL droplets and/or globules of DNAPL trapped in the soil interstices by capillary forces, preventing further migration. If, however, the amount of DNAPLs released exceeds the "absorptive" capacity of the vadose zone to hold DNAPLs in the form of residual saturation, the migrating DNAPLs will reach the ground water table and the associated capillary fringe.

Being heavier than water, DNAPLs have a natural tendency to sink through the ground water table. However, being immiscible in water, in order to sink into the saturated zone, DNAPLs must in essence "push" the water out of the way in order to intrude into the pore spaces originally occupied by ground water. To do this, they must overcome the capillary pressure or "displacement pressure" associated with the interfacial tension between the DNAPLs and ground water. In simple terms, displacement pressures in medium- to coarse-grained sand aquifers, because of large pore sizes, are typically quite low and allow relatively unimpeded intrusion of DNAPLs into such aquifers. The displacement pressure in fine-grained strata such as silts and clays, however, can be high enough to allow them to serve as barriers to vertical DNAPL migration. The displacement pressure of even fine-grained sands can be sufficiently high to arrest the vertical migration of an advancing DNAPL front and to promote lateral spreading of the DNAPLs atop the finer-grained layer.

Once the DNAPLs have overcome displacement pressures and intrude into the saturated zone, they will continue migrating generally downward through the saturated zone with their migration still primarily controlled by capillary phenomenon. Consequently, any stratification, however slight, in the saturated portions of the aquifer can lead to complex patterns of DNAPL migration. If sufficiently fine-grained strata are encountered, "pools" may also form atop these strata. In a "pool", DNAPLs might occupy from 40 to 70 percent of the pore space of the porous medium.

In the same manner as in the vadose zone, the intruding DNAPLs leave behind a residual saturation of small droplets and globules in the saturated porous medium through which they have intruded. The net result is that the aquifer, like the vadose zone, has a certain capacity to hold and thereby arrest the further

vertical migration of a DNAPL chemical. If, however, a sufficient volume of DNAPLs has been released, they may exceed the "carrying" capacity of the aquifer and DNAPLs will begin to accumulate atop the underlying aquitard in the form of a pool or a series of small pools or puddles.

The behavior of pools of DNAPLs is fundamentally different than the zones of residual saturation, which are composed of innumerable disconnected droplets and globules. In a pool of DNAPLs, much of the soil's pore spaces are filled with DNAPLs, such that DNAPLs are the connected phase. As the connected phase, pure phase DNAPL flow is possible, provided sufficient DNAPL head gradients exist. Therefore, if the top of the aquitard slopes, the DNAPL pool may flow down dip along the top of the aquitard. The flow of a DNAPL pool in this manner is controlled almost exclusively by the structure of the geologic system rather than by ground water flow directions. Consequently, the pool of DNAPL will flow down dip on the aquitard's surface even if ground water flows in the opposite direction.

The potential for flow of a DNAPL pool along an aquitard's surface is finite, because as it flows it leaves behind a trail of residual saturation within the aquifer. As a result, the degree of DNAPL saturation within a pool will be gradually reduced until DNAPLs are no longer a connected phase and are therefore no longer capable of separate phase flow.

Potential DNAPL Source Areas

The site consists of 12 potential contaminant source areas (generalized), as identified by USEPA under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA). The potential source areas represent those areas that may contain, and potentially release, contaminants to the subsurface based on former site activities. These activities include the former manufacturing processes, material handling, and disposal practices. Since each of these areas was considered to be a potential contaminant source area, they were all included as potential DNAPL source areas also. These potential DNAPL source areas possess varying degrees of DNAPL likelihood, ranging from "highly improbable" to "probable". However, to provide an unbiased evaluation of the source areas, they were all evaluated with the same rigor. The potential DNAPL source areas are illustrated on Figure 1, with the areas being labeled A through L.

Methods of DNAPL Investigation

The identification and delineation of DNAPLs in the subsurface have proven to be arduous if not elusive tasks at many suspected DNAPL sites. Often, physical evidence doesn't lend itself to the direct identification of DNAPLs; therefore the use of indirect methods must be relied upon. An integrated approach has been developed to assess a site for the potential presence and distribution of DNAPLs using existing site data. Both soil and ground water quality data were evaluated to determine the potential presence of DNAPLs using various indirect screening methods. Ground water quality data were evaluated using the USEPA guidance procedures, which suggest that if a compound's measured concentration is greater than one percent of its upper solubility limit, then the presence of DNAPL is likely. Soils were evaluated by a method after Feenstra et al. (1991), which allows for a comparison of soil quality data to calculated threshold concentrations for the identification of DNAPLs. A site-specific head-space correlation was developed and visual observations were used. The history of site operations was also reviewed in terms of locations of former manufacturing processes, materials storage/handling, and on-site disposal. The methodology and application of the screening methods are discussed in greater detail in the following sections.

The screening methodologies employed in this case study do not readily differentiate DNAPLs from LNAPLs. Therefore, the methodologies in essence are screening for NAPLs (non-aqueous phase liquids) in general. Since DNAPLs are the primary chemicals of concern at the study site, they will be the focus of this discussion; however, the terms DNAPLs and NAPLs could be used interchangeably in many instances.

Review of Site History

The review of historical site information can play a significant part in assessing the potential occurrence of DNAPLs at a site or area within a site. Site evaluation flow charts presented in EPA's DNAPL delineation guidance (USEPA, 1992) pose the following questions:

1. Does the industry type suggest a high probability of historical DNAPL release?
2. Does a process or waste practice employed at the site suggest a high probability of historical DNAPL release?
3. Were any DNAPL-related chemicals used in appreciable quantities at the site?

A positive response to any of these questions would result in the evaluation of available site characterization data to assess the potential occurrence of DNAPLs at the site. These criteria were applied to assess the 12 potential DNAPL source areas at the site. The results are presented in Table 1.

Ground Water Quality Evaluation

Ground water quality data can be used to indirectly infer the presence of a DNAPL source in the subsurface. This technique involves direct comparison of the measured chemical concentration in ground water to the chemical's upper solubility limit. The upper solubility limit refers to the maximum concentration of a pure-phase DNAPL that will dissolve in distilled water at a particular temperature. If a DNAPL is comprised of a mixture of chemicals, the upper solubility limit of a particular compound should be approximately proportional to the mole fraction of that chemical. This mole fraction-based concentration is termed the effective solubility limit.

When a DNAPL comes in contact with water and is allowed to equilibrate in the laboratory, the maximum chemical concentration that will be observed for a given sample at a given temperature is governed by the DNAPL's upper solubility limit. However, when a DNAPL is released to the subsurface and allowed to equilibrate with ground water, the chemical concentration detected is generally less than 10 percent of the solubility limit. This may result from the effects of non-uniform ground water flow, variable DNAPL distribution, water salinity, and the mixing of ground water in a well (Cohen and Mercer, 1993). Other factors might include DNAPL aging processes and whether or not the DNAPL is accessible to flowing ground water. Additionally, reductions in solubility limits (i.e., effective solubility) due to a multi-component DNAPL mixture may also contribute to the lower concentrations detected in the ground water sample.

The EPA's guidance (USEPA, 1992) suggests that if a compound's measured concentration in ground water is greater than 1 percent of its upper solubility limit, or effective solubility limit (in the case of mixed component DNAPLs), then a DNAPL source may be present at the site. This does not imply, however, that DNAPL is present at the particular well location measured. Instead, the EPA guidance describes the use of this criterion to establish "conditions that indicate the potential for DNAPL at the site based on laboratory data." It would be more appropriate to describe a 1 percent exceedance as indicative of a

possible DNAPL source at, or upgradient of, the measured location. This distinction indicates that the use of this guidance to define the precise lateral extent of DNAPLs, is outside the proper applicability of this screening process.

As noted previously, if a DNAPL mixture is present, the dissolved phase equilibrium concentrations (i.e., effective solubility limits) of the individual compounds are generally lower than the pure-phase upper solubility limit. As a result, the effective solubility limit should be used to screen sites for the possible presence of DNAPLs rather than the upper solubility limit. For mixtures of liquid chemicals, the effective solubility can be estimated by the following equation:

$$S_i^e = X_i S_i \quad \text{Equation 1}$$

Where S_i^e is the effective solubility of constituent i ($\mu\text{g/L}$), X_i is the mole fraction of constituent i in the DNAPL mixture, and S_i is the pure-phase upper solubility limit of constituent i ($\mu\text{g/L}$) (Feenstra et al., 1991). The relationship is approximate and does not account for non-ideal behavior of mixtures such as co-solvency, etc.

The methodology was applied to over 7,000 analytical ground water samples collected from over 400 monitoring wells on site. The compounds of interest included all detected organic compounds that were on the target compound list for the respective analyses. The associated upper solubility limits for the detected compounds were those recommended by USEPA. The use of 1 percent of the upper solubility limit as a direct comparison assumes that the DNAPL present is a single pure-phase DNAPL. DNAPL mixtures would be expected to yield lower concentrations for individual compounds. Since historical information, as well as soil and ground water analytical data, suggest that the DNAPL present at the site would, for the most part, likely be comprised of a mixture of chemicals, the use of 1 percent of the upper solubility limit may overlook potential indications of DNAPL sources. However, the use of effective solubility to detect potential DNAPLs is complicated by the inherent difficulties with determining accurate mole fractions for individual components of the mixture. This is generally accomplished by obtaining samples of the DNAPL and determining its fractional composition by analytical methods. DNAPL mixtures' fractional compositions may also be estimated from site historical records. To date, no free-phase DNAPLs have been observed at the site in sufficient quantities to sample. Various indirect methods were evaluated to estimate the mole fraction of the DNAPL constituents at the site. However, since there are multiple potential DNAPL source areas contributing to the ground water plume at the site, it was determined that no method evaluated could accurately determine mole fractions to meaningfully screen ground water analytical data for the entire site. However, the importance of recognizing that a multi-constituent DNAPL mixture likely exists at the site was not ignored when evaluating available ground water quality data. Due to the variability in estimating mole fractions of DNAPL mixture constituents that could be applied to the entire site, a sensitivity analysis was performed assuming arbitrary mole fractions of 20 percent, 15 percent, 10 percent, 5 percent, and 2 percent for each compound. The upper solubility limit, or 100 percent mole fraction, was also used in the analysis for comparison. Whereas using the upper solubility limit assumes that each compound is present as a single-component DNAPL, the 2 percent mole fraction assumption assumes that there is a DNAPL mixture, and that each detected compound comprises 2 percent of the total. The assumed mole fractions between 2 and 100 percent represent a gradational variation between the two extremes.

The USEPA guidance methodology previously discussed was then applied to the ground water quality analytical data from the site. The results for the upper solubility limit analysis, and the results for the

effective solubility limits analyses based on 20 percent and 2 percent mole fractions are discussed in the following paragraphs.

A total of 50 monitoring wells were identified that suggested a DNAPL source was at or upgradient of the well locations. These wells possessed at least one compound detected during at least one sampling event that exceeded 1 percent of the upper solubility limit. The spatial distribution of these wells (see Figure 3) is within the identified ground water contaminant plume. Based on a 20 percent assumed mole fraction, a total of 75 wells were identified with at least one exceedance of 1 percent of the effective solubility limit. Again, the spatial distribution of these wells (see Figure 3) roughly coincides with the identified ground water contaminant plume, with the exception of a few anomalous locations which were triggered by sporadic, low-level detections. Based on a 2 percent assumed mole fraction, a total of 147 wells were identified with at least one exceedance of 1 percent of the effective solubility limit. Though the most conservative scenario, the spatial distribution of these wells again roughly coincides with the identified ground water plume. However, since this scenario assumes that each compound constitutes only 2 percent of the DNAPL mixture, the total number of wells indicating the possible presence of DNAPLs increased by a factor of approximately 2, as compared to the 20 percent mole fraction scenario.

As Figure 3 illustrates, several of the assumed 2 percent mole fraction exceedances were from wells remote from the ground water contaminant plume, with a couple of wells even being located east of the Toms River (ground water flows towards the river from both sides). For many of these locations, the compound(s) that exceeded 1 percent of the effective solubility limit were generally very low solubility organic compounds, resulting in such low effective solubility limits that 1 percent of that limit was at or below the method detection limit. This resulted in exceedances during the screening process for detections in the low part per billion range that in reality could be attributed to laboratory artifacts or variability, and are not indicative of a DNAPL source.

In summary, almost three times as many wells were flagged for the 2 percent mole fraction scenario as compared to the upper solubility limit scenario. However, the overall distribution of the identified wells did not change, nor were any legitimate additional source areas identified. The lower assumed effective solubility limits tended to dilute the screening utility of the method and did not significantly aid in the determination of a unique mole fraction scenario that should be used for the site.

Soil Quality Evaluation

Analytical soil samples are routinely collected to evaluate the presence of volatile and semi-volatile organic compounds in soils. The organic analysis of these soil samples, however, generally determines the total chemical mass per unit dry weight of soil sample and does not differentiate as to whether the constituent was adsorbed to the soil, dissolved in the pore water, volatilized in soil gas, or present as DNAPL. Feenstra, et al. (1991) developed a technique to assess the potential presence/absence of residual DNAPLs in soils based on the organic compound concentrations in soil samples. Their method uses the physical and chemical properties of the soil to estimate the maximum theoretical concentration of a particular compound within the pore water for both saturated and unsaturated soils. The method assumes that no DNAPLs are present in the soil. For a given soil sample, there is a maximum total soil concentration defined by the solubility of the chemical in soil water, the saturated soil-gas concentration, and the sorption capacity of the solids, that can be contained in the soil if no DNAPLs are present. The solubilities of the individual chemicals are then used as means for assessing the presence of DNAPLs. If the calculated pore water concentration exceeds the upper/effective solubility limit for that compound, then residual DNAPLs are likely to be present.

The pore water concentration for the unsaturated zone and water saturated zone is calculated by the following equations (Feenstra et al., 1991):

Unsaturated Zone:

$$C_w = \frac{C_t \rho}{(K_d \rho + \Phi_w + H_c \Phi_a)} \quad \text{Equation 3}$$

Saturated Zone:

$$C_w = \frac{C_t \rho}{K_d \rho + \Phi_w} \quad \text{Equation 4}$$

Where:

- C_w = chemical concentration of contaminant in pore water (ppm)
- C_t = total soil chemical concentration of contaminant (ppm)
- ρ = dry bulk density of the soil (g/cm³)
- Φ_w = water-filled porosity (fraction of the porous medium volume)
- Φ_a = air-filled porosity (fraction of the porous medium volume)
- H_c = Henry's Law constant (dimensionless)
- K_d = partition coefficient between pore water and soil solids (cm³/g)
 $K_d = K_{oc} f_{oc}$
 K_{oc} = organic carbon-water partition coefficient (cm³/g)
 f_{oc} = fractional organic carbon in soil

To employ this method, the chemical concentrations detected in each soil sample are used to calculate the associated pore water concentrations for comparison to the upper/effective solubility limits for the chemical compounds of interest. As can be surmised, with a large number of soil samples and multiple detected chemical constituents, this can be a sizable task. To streamline the soil screening process, Equations 2 and 3 can be rearranged to solve for C_t :

Unsaturated Zone:

$$C_t = \frac{(K_d \rho + \Phi_w + H_c \Phi_a) (C_w)}{\rho} \quad \text{Equation 5}$$

Saturated Zone:

$$C_t = \frac{(K_d \rho + \Phi_w) (C_w)}{\rho} \quad \text{Equation 6}$$

Assuming C_w is equal the upper/effective solubility limit, C_t then becomes the threshold soil concentration for a particular contaminant above which the presence of residual DNAPLs in the soil is likely. Again, if a DNAPL mixture is present, then the effective solubility limit, as opposed to the upper solubility limit, should be used in the evaluation of soils for the possible presence of residual DNAPLs. The methodology

for estimating the effective solubility was presented in the previous section. The mole fraction sensitivity analysis employed for the ground water quality evaluation was also applied to the soil quality evaluation.

The available soil analytical data from the site were reviewed for indications of the possible presence of residual DNAPLs. This was completed by calculating threshold soil concentrations using equation (5) for the 22 compounds presented in Table 2. These compounds are considered representative of the major potential DNAPL components at the site based on frequency of detection, concentrations detected, and historical records of site operations. Several of the 22 compounds are LNAPLs rather than DNAPLs; however, the screening methods used apply to both, so no special differentiation was made. For screening purposes, the unsaturated zone threshold concentrations were used, which are lower in concentration than the threshold concentrations in the saturated soils. Additionally, the upper and effective solubility limits (based on a 20 percent, 15 percent, 10 percent, 5 percent, and 2 percent mole fractions) were used to calculate the threshold concentrations. The basic assumptions were that the water-filled pore volume in the unsaturated zone is 10 percent (based on average moisture content for analytical soil samples collected at the site), while the air-filled pore volume is 20 percent of the total soil volume (based on an average total porosity of 30 percent). The bulk density for the sandy soil was estimated at 1.8 g/cm³. [Typical bulk density for a fine to coarse sand ranges from 1.4 g/cm³ to 2.2 g/cm³ (Lambe, 1969)]. The organic carbon-water partition coefficients were calculated using the Chiou et al. (1979) or Karickhoff et al. (1979) relationships, depending on which relationship was deemed most appropriate for a particular compound, and were based on the upper solubility limits. The average fractional organic carbon (f_{oc}) in the sandy soil was determined to be 0.13 percent (based on representative analyses from site soils). The upper solubility limits, Henry's Law Constants, K_{oc} , and K_d coefficients for the respective compounds are presented in Table 2. The associated threshold concentrations for the various mole fractions are also presented in Table 2.

More than 1,200 soil sample analytical results were evaluated during the soil quality sensitivity analysis. As a result of this, those areas which were identified as having potential residual DNAPLs were evaluated on an individual basis to assess the likelihood of DNAPLs actually being present. The total number of samples per source area versus the number of samples that exceed the soil threshold concentrations are presented on Table 3. As with the mole fraction sensitivity analysis for ground water, the soil sensitivity analysis did not yield a unique mole fraction that could be applied on a site-wide basis. However, the results of this evaluation did yield a fairly realistic view of the possible distribution of DNAPLs at the site.

Head-Space Correlation

At many sites, a considerable number of head-space analyses are routinely performed to screen soils for volatile organics. The use of these data has been evaluated by Cohen, et al. (1992) as a possible screening tool to infer the presence of residual NAPL in soils. Cohen's work suggests that head-space analysis performed with standard field instrumentation can potentially be used as a tool in screening soils for the possible presence of NAPL (field screening instruments typically cannot differentiate DNAPL and LNAPL compounds). For the study site, over 5,000 head-space results (measured by either an HNu Systems photoionization detector, or "HNu", or an organic vapor analyzer, or "OVA") were available, including samples from hundreds of different soil borings located within the potential DNAPL source areas and throughout the site. For most of these head-space samples, no corresponding analytical results exist. However, 97 soil samples were identified for which both analytical data and head-space analysis (measured by an HNu) were collected. To determine the possible presence of residual NAPL, each soil sample was evaluated using the method of Feenstra, et al. (1991), assuming a threshold concentration calculated using the upper solubility limit. The 23 samples with potential NAPL identified with that method had a mean HNu head-space reading of 332 ppm_v, as compared to the 74 samples without potential residual NAPL,

which had a mean HNu reading of 95 ppm_v. As expected, there was an overlap in head-space concentration between samples with and without potential NAPL. However, it was found that 87 percent of all samples with potential residual NAPL had HNu readings of 100 ppm_v or higher. Thus, using 100 ppm_v as a NAPL screening threshold could be expected to capture all but about 13 percent of samples with potential residual NAPL, and would only incorrectly identify 6 percent of the samples as having residual NAPL that in fact did not. Given the inherent variability in head-space analyses, a NAPL head-space screening threshold of 100 ppm_v was considered more than adequate.

A separate correlation for head-space results obtained using an OVA, rather than HNu, was not established because many OVA readings were off scale (i.e., >1,000 ppm_v). This made it difficult to confidently establish an accurate NAPL screening threshold concentration with well-defined limits. However, since the OVA generally was more sensitive to organic vapor concentrations than the HNu, applying the HNu screening threshold to the OVA values (for results where only an OVA was used) would result in identifying more samples with possible residual NAPL. The use of the OVA data was deemed appropriate for the purpose of screening all the available head-space results and minimizing any "missed" DNAPL zones.

A screening threshold concentration of 100 ppm_v was applied to all available head-space data, (HNu and OVA) for the site. Utilizing this head-space/residual NAPL correlation as a screening tool offered the opportunity to expand the residual NAPL definition efforts at the site. Although actual analytical results for soil samples were generally limited to the immediate vicinity of the potential source areas, head-space data were available from a widespread number of locations throughout the site.

The results of the head-space analyses screening are presented in Table 1. In general, the head-space results indicate that the possible presence of residual NAPL (HNu values greater than 100 ppm_v) is limited in lateral extent to the potential DNAPL source areas. The sporadic boring locations indicating the possible presence of residual NAPL outside of these areas are considered to be artifacts associated with false positive identification and the inherent variability in field instruments used from person to person, study to study, and year to year.

Visual Observations

The final technique used to screen the subsurface soil for the possible presence of residual DNAPLs was to review all visual inspection data collected in the field. The visual inspections were routinely performed during installation of the monitoring wells and soil borings at the site. The technique consisted of reviewing soil boring logs and field notes, and searching for descriptions and observations indicating the possible presence of DNAPLs. The results of this evaluation indicated that 24 boring locations were flagged as possible DNAPL locations. Each of these locations were within or adjacent to suspected DNAPL source areas. Those locations suggesting the possible visual evidence of DNAPLs are based on recorded field observations such as discoloration, texture, odors, etc. However, because the objective at the time these observations were made was not specifically to define the presence or absence of any DNAPLs, interpretation inconsistencies between data sets likely exists and may effect the quality of these results. Noteworthy is the fact that the visual observation method could not be depended upon to infer the presence of DNAPLs in all the same areas as identified by some of the other screening methodologies. This underscores the difficulty in directly identifying DNAPLs or residual DNAPLs in the field. The results of the visual observations are presented in Table 1.

Distribution of Potential DNAPLs

The results of the ground water quality, soil quality, head-space, and visual observation evaluations allow for the inference of the general extent of potential DNAPLs at the site with some degree of confidence. The results are summarized on Table 1. The potential DNAPL source areas that may actually contain DNAPLs were determined to be Areas A, B, C, D, E, F, H, and J. Of these, Areas A, F, and H are considered to be the primary DNAPL source areas, indicating strong evidence of widespread residual DNAPLs. The remaining areas are considered secondary source areas, indicating only sporadic and localized evidence of DNAPLs. The secondary DNAPL source areas are not considered to be long-term environmental risks.

The apparent lateral extent of any potential residual DNAPLs contained in the subsurface soil is, for the most part, limited to their source areas. The apparent lack of widespread lateral migration is supported by consideration of likely physical DNAPL transport mechanisms. The major transport mechanism would be migration downward and laterally in response to structural trends. Some major structural trends that would control the lateral migration are the upper surfaces of the less permeable Yellow Clay, Cohansey/Kirkwood Transitional Aquitard, and the Upper Kirkwood Aquitard. Although the Yellow Clay is not continuous, it could support localized migration of DNAPLs at the site. The data did not indicate any strong evidence of DNAPLs outside of the DNAPL source areas.

The vertical distribution of residual DNAPLs at the site was evaluated based on the existing data. The data suggest that vertical migration of DNAPLs beneath their source areas has not extended beneath the Cohansey/Kirkwood Transitional Aquitard. Where the Yellow Clay is present, vertical migration appears to terminate at the clay surface. In general, vertical migration is limited to the first resistant stratigraphic unit encountered. The units below the Cohansey/Kirkwood Transitional Aquitard did not indicate any strong evidence of residual DNAPLs. The DNAPLs, where present, have apparently migrated to the first resistant layer then have begun to migrate short distances laterally while also slightly penetrating the resistant layer, partially filling pore spaces along their path.

Summary

An integrated approach was developed for assessing the potential presence and distribution of DNAPLs at a Superfund site in New Jersey. The approach was comprised of empirical, analytical, observational, and anecdotal components and was applied to the existing database of environmental data compiled for the site. The integrated methodology was successful in identifying those areas with the greatest potential for DNAPLs, and the approximate three-dimensional distribution of DNAPLs within those areas. Capitalizing on the utility of existing data allowed the scope of future investigative efforts to be streamlined with respect to further delineation of DNAPL zones at the site. Such a delineation is essential when considering source area remedial technologies and the practicability of remediating DNAPL source areas. The integrated approach for assessing potential DNAPLs at the case study site, as well as the streamlined scope of work for additional investigation, was accepted and approved by USEPA. Approaches similar to the one used in this case study could be developed for other sites where DNAPLs are suspected and a broad database of environmental data already exists.

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TABLE 1: SUMMARY OF DNAPL ASSESSMENT

Potential DNAPL Source Area	Potential for DNAPL Presence					Overall Potential for DNAPL
	Based on Review of Site History	Based on Evaluation of Ground Water Quality Data	Based on Evaluation of Soil Quality Data	Based on Evaluation of Head-Space Analyses	Based on Visual Observations	
A	High	High	High	Moderate	Moderate	High
B	Low	Low	Moderate	Low	Moderate	Low
C	Low	Low	Moderate	Moderate	Moderate	Moderate
D	Low	Low	Moderate	Low	Moderate	Low
E	Moderate	Low	Moderate	Low	Low	Low
F	High	High	Moderate	Moderate	High	High
G	Low	Low	Low	Low	Low	Low
H	High	High	High	High	High	High
I	Moderate	Moderate	Low	Low	Low	Low
J	Moderate	Low	Moderate	Low	Low	Low
K	Low	Low	Low	Low	Low	Low
L	Low	Low	Low	Low	Low	Low

TABLE 2: PROPERTIES OF POTENTIAL NAPL COMPOUNDS

Compound	Henry's Law Constant (dimensionless)	Solubility Limit (mg/l)	K _{oc} (ml/g)	K _d (ml/g)	Threshold Concentration (µg/kg)
Anthracene	2.71E-03	75	66,830	86.9	6,520
Benzene	2.28E-01	1,780,000	186	0.241	573,722
Chlorobenzene	1.87E-01	490,000	178	0.231	150,743
2-Chloronaphthalene	2.55E-02	6,740	5,604	7.29	49,498
2-Chlorotoluene	2.60E-01	72,000	553	0.719	57,815
4-Chlorotoluene	7.08E-01	44,000	727	0.945	47,498
1,2-Dichlorobenzene	4.99E-02	100,000	500	0.650	71,147
1,3-Dichlorobenzene	1.96E-01	69,000	615	0.800	60,511
1,4-Dichlorobenzene	1.87E-01	80,000	566	0.736	65,024
Ethylbenzene	2.75E-01	152,000	828	1.076	176,612
Naphthalene	1.91E-02	31,000	2,162	2.81	88,919
Nitrobenzene	1.02E-03	1,900,000	229	0.298	671,865
Phenanthrene	1.07E-03	1,180	15,090	19.6	23,214
1,1,2,2-Tetrachloroethane	1.90E-02	2,900,000	83	0.107	478,446
Tetrachlorethene	6.37E-01	150,000	427	0.555	102,181
Toluene	2.79E-01	515,000	155	0.201	148,201
1,2,4-Trichlorobenzene	9.57E-02	19,000	3,398	4.42	85,176
Trichloroethene	3.79E-01	1,000,000	130	0.169	267,067
1,2,3-Trichloropropane	1.32E-02	1,750,000	102	0.132	331,275
Xylenes, total	2.93E-01	189,000	293	0.381	88,581
o-Xylene	2.19E-01	170,000	311	0.404	82,218
p- & m-Xylene	2.96E-01	200,000	284	0.369	91,432

TABLE 3: TOTAL NUMBER OF SOIL SAMPLES VERSUS NUMBER OF SAMPLES THAT EXCEED THE SOIL THRESHOLD CONCENTRATIONS

Potential DNAPL Source Area	Total Number of Samples	Number of Samples with at Least One Threshold Concentration Exceedance					
		Mole Fraction Percent					
		100%	20%	15%	10%	5%	2%
A	409	6	9	10	10	13	20
B	111	2	2	2	2	2	6
C	41	1	3	3	3	4	6
D	99	2	4	6	7	9	10
E	37	3	6	6	7	7	11
F	188	16	28	33	37	39	51
G	12	0	0	0	0	0	0
H	260	43	60	64	68	74	74
I	19	0	0	1	2	3	5
J	35	1	1	1	1	3	5
K	7	0	0	0	0	0	0
L	8	0	0	0	0	0	0

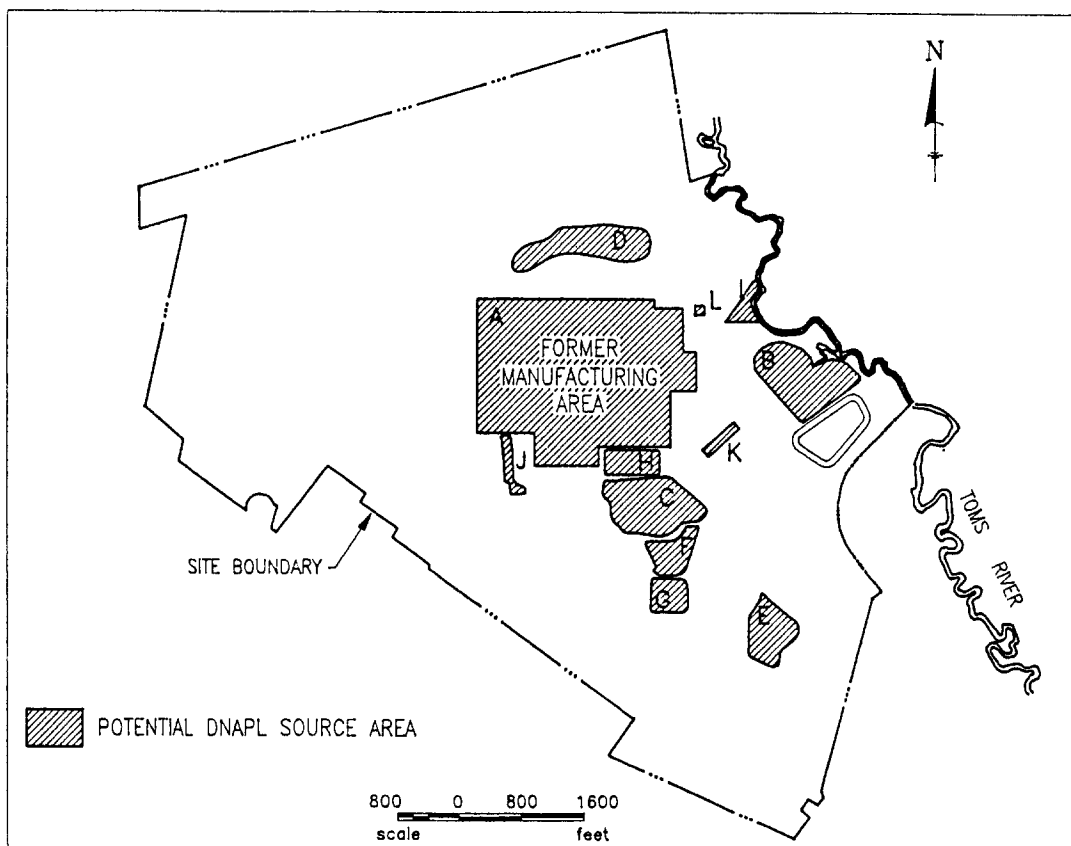


FIGURE 1: SITE PLAN SHOWING POTENTIAL DNAPL SOURCE AREAS

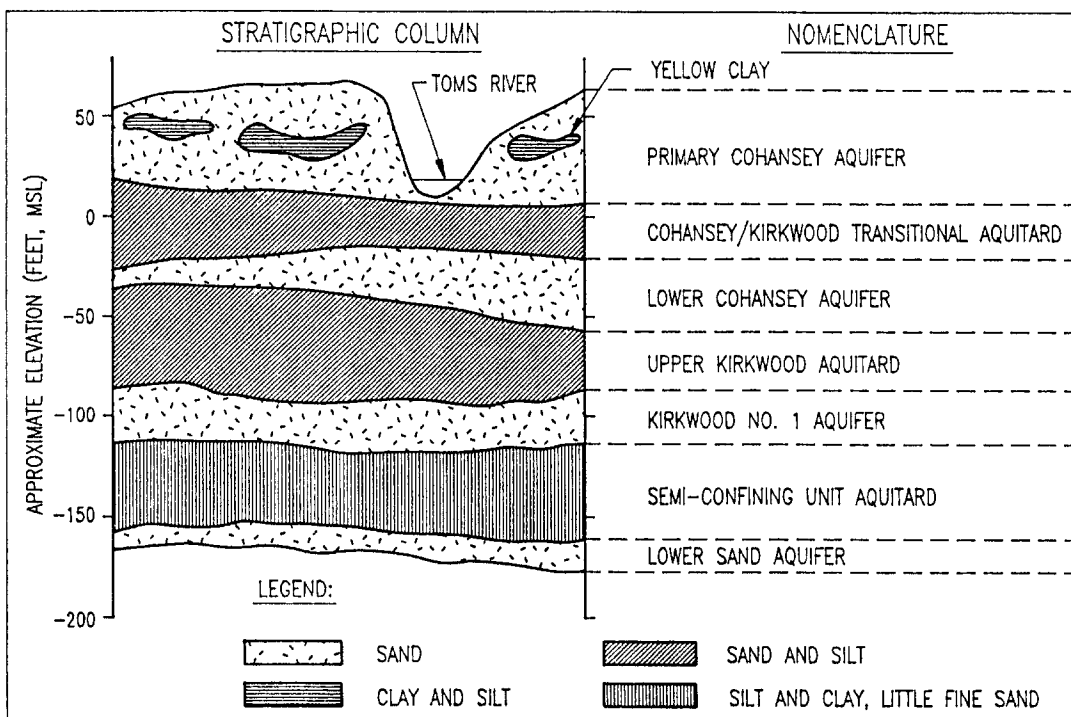


FIGURE 2: GENERALIZED SITE STRATIGRAPHY AND NOMENCLATURE

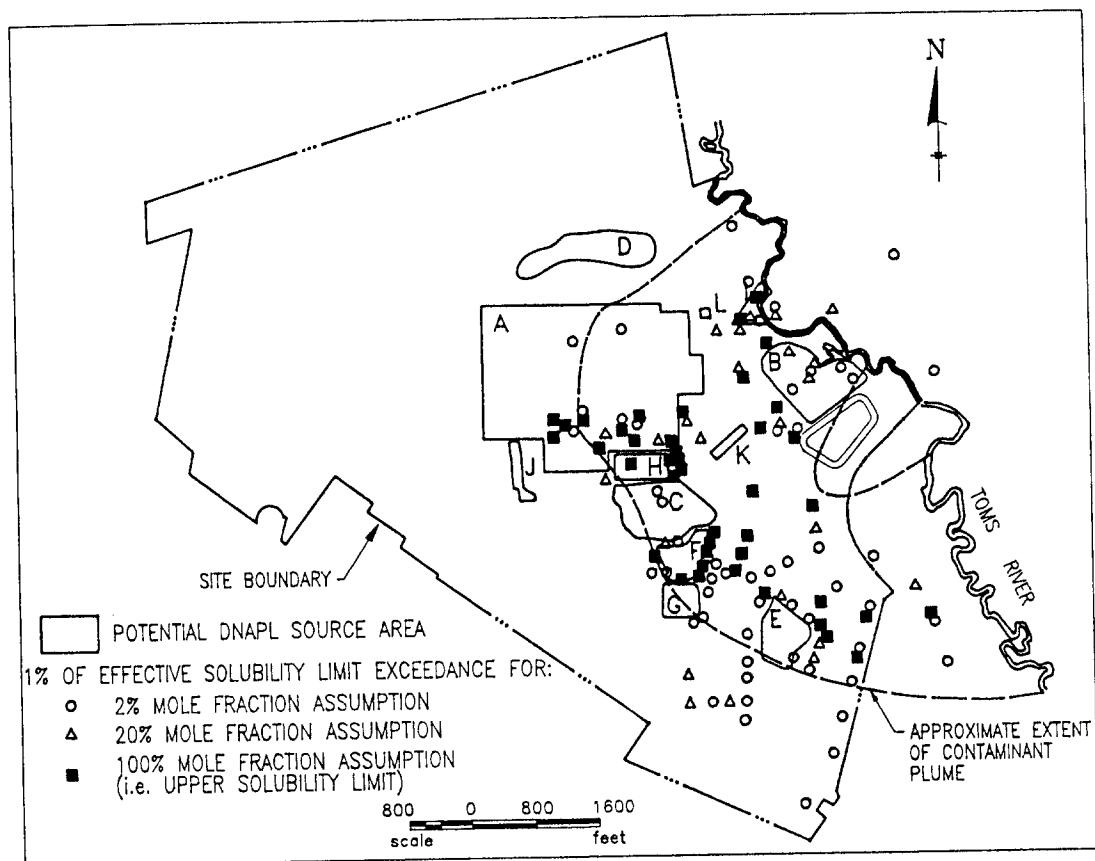


FIGURE 3: SUMMARY OF GROUND WATER QUALITY EVALUATION MOLE FRACTION SENSITIVITY ANALYSIS

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